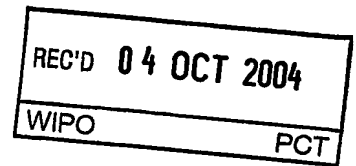




Europäisches
Patentamt

European
Patent Office

Office européen
des brevets



Bescheinigung

Certificate

Attestation

Die angehefteten Unterlagen stimmen mit der ursprünglich eingereichten Fassung der auf dem nächsten Blatt bezeichneten europäischen Patentanmeldung überein.

The attached documents are exact copies of the European patent application described on the following page, as originally filed.

Les documents fixés à cette attestation sont conformes à la version initialement déposée de la demande de brevet européen spécifiée à la page suivante.

Patentanmeldung Nr. Patent application No. Demande de brevet n°

03076591.1

**PRIORITY
DOCUMENT**
SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH RULE 17.1(a) OR (b)

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

R C van Dijk



Anmeldung Nr:
Application no.: 03076591.1
Demande no:

Anmeldetag:
Date of filing: 23.05.03
Date de dépôt:

Anmelder/Applicant(s)/Demandeur(s):

DSM IP Assets B.V.
Het Overloon 1
6411 TE Heerlen
PAYS-BAS

Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:
(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.
If no title is shown please refer to the description.
Si aucun titre n'est indiqué se référer à la description.)

Continuous process for preparing caprolactam

In Anspruch genommene Priorität(en) / Priority(ies) claimed / Priorité(s)
revendiquée(s)
Staat/Tag/Aktenzeichen/State/Date/File no./Pays/Date/Numéro de dépôt:

Internationale Patentklassifikation/International Patent Classification/
Classification internationale des brevets:

C07D201/00

Am Anmeldetag benannte Vertragstaaten/Contracting states designated at date of
filing/Etats contractants désignées lors du dépôt:

AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IT LU MC NL
PT RO SE SI SK TR LI

PE 21511

- 1 -

CONTINUOUS PROCESS FOR PREPARING CAPROLACTAM

5

The invention relates to a continuous process for preparing caprolactam by Beckmann rearrangement of cyclohexanone oxime, said process comprising

- a) feeding (i) oleum and (ii) cyclohexanone oxime into a first reaction mixture comprising caprolactam, sulfuric acid and SO_3 ,
- 10 b) feeding (iii) a portion of the first reaction mixture and (iv) cyclohexanone oxime into a second reaction mixture comprising caprolactam, sulfuric acid and SO_3 ,
- c) withdrawing a portion of the second reaction mixture.

Caprolactam can be prepared by Beckmann rearrangement of cyclohexanone oxime. Such Beckmann rearrangement can be carried out by admixing cyclohexanone oxime to a reaction mixture comprising caprolactam, sulfuric acid and SO_3 . In such process the sulfuric acid and SO_3 is a catalyst for the conversion of cyclohexanone oxime towards caprolactam. Such conversion is known to occur instantaneously.

20

Such a process is described in US-A-3953438. In this process cyclohexanone oxime containing 4.9 wt.% water and oleum containing 25 weight percent SO_3 are continuously fed to a first rearrangement zone containing a circulating reaction mass such that the circulating reaction mass having a sulfuric acid + SO_3 to caprolactam weight ratio of 1.45 and a SO_3 content of 5.9 weight percent. A portion of the reaction mass of the first catalytic rearrangement zone equivalent to the feed thereto is continuously removed and fed to a second rearrangement zone containing a circulating reaction mass. Cyclohexanone oxime containing 4.9 wt.% water is also continuously fed to the circulating reaction mass of the second rearrangement zone. The circulating reaction mass of the second rearrangement zone has a sulfuric acid + SO_3 to caprolactam weight ratio of 1.14 and a SO_3 content of 3.2 weight percent. A portion of the reaction mass of the second catalytic rearrangement zone equivalent to the feed thereto is withdrawn.

25

30

In US-A-3953438 it is described that the oxime may contain up to 6 wt.% water. Although a value of 0.1 wt.% water is mentioned as a lower limit, in fact, the process disclosed in this patent is carried out at high water content, i.e. in all the examples oxime containing 4.9 wt.% of water is used. No method is given how to reduce the water content of the oxime.

35

- 2 -

In the process of US-A-3953438 oleum having relatively high oleum strength is needed. Hence large quantities of SO_3 are needed to obtain the desired yield to caprolactam.

The object of the invention is to improve the yield while using relatively small amounts of SO_3 .

This object is achieved in that the process further comprises obtaining the cyclohexanone oxime that is fed to the first reaction mixture and second reaction mixture by:

- a) preparing an organic medium comprising cyclohexanone oxime dissolved in an organic solvent
- b) separating, by distillation, cyclohexanone oxime from said organic medium

It has been found that with the process of the present invention less SO_3 needs to be added for obtaining a high yield to caprolactam. Adding high quantities of SO_3 is disadvantageous, since, either a high SO_3 concentration in the oleum ($\text{H}_2\text{SO}_4/\text{SO}_3$ mixture) has to be applied, which is disadvantageous from an economical point of view and because the risk of fuming of the oleum increases and because the flowability of the oleum decreases or, when still using a relatively low concentration of SO_3 in the oleum, high quantities of oleum has to be fed to the rearrangement mixture per quantity of oxime, which results in the formation of high amounts of by-product (ammonium sulfate) during subsequent neutralization.

In the process of the present invention either a higher yield to caprolactam can be obtained for a given amount of SO_3 added to the process, or less SO_3 needs to be added to obtain a given yield to caprolactam. In addition, with the process of the invention either an improved quality of the obtained caprolactam can be obtained for a given amount of SO_3 added to the process, or less SO_3 needs to be added to obtain a given quality to caprolactam.

The cyclohexanone oxime introduced into the reaction mixture is obtained by:

- a) preparing an organic medium comprising cyclohexanone oxime dissolved in an organic solvent
- b) separating, by distillation, cyclohexanone oxime from said organic medium.

Preparing an organic medium comprising cyclohexanone oxime dissolved in an organic solvent is preferably carried out by contacting in a reaction zone in countercurrent flow a stream of a solution of cyclohexanone in an organic solvent which is also a solvent for the cyclohexanone oxime and a stream of an a

- 3 -

phosphate buffered, aqueous solution of hydroxylammonium; and withdrawing from the reaction zone an organic medium of cyclohexanone oxime dissolved in said organic solvent. Particularly suitable organic solvent for use in the process for preparing cyclohexanone oxime are toluene and benzene. Preferably toluene is used as organic solvent. The phosphate buffered, aqueous reaction medium is preferably continuously recycled between a hydroxylammonium synthesis zone and a cyclohexanone oxime synthesis zone. In the hydroxylammonium synthesis zone hydroxylammonium is formed by catalytic reduction of nitrate ions or nitric oxide with hydrogen. In the cyclohexanone oxime synthesis zone, hydroxylammonium formed in the hydroxylammonium synthesis zone reacts with cyclohexanone to form cyclohexanone oxime. The cyclohexanone oxime can then be separated from the aqueous reaction medium which is recycled to the hydroxylammonium synthesis zone. An organic medium comprising the formed cyclohexanone oxime dissolved in said organic solvent is withdrawn from the reaction zone, and distilled to recover cyclohexanone oxime having a water content less than 1 wt.%, preferably even less than 0.1 wt.%. Cyclohexanone oxime is preferably fed to the reaction mixture in the form of a liquid melt.

The SO_3 concentration of the reaction mixtures comprising caprolactam, sulfuric acid and SO_3 is preferably higher than 6 wt.%, more preferably higher than 8 wt.% and even more preferably higher than 10 wt.%. For practical reasons the SO_3 content of the reaction mixture of the reaction mixtures is usually lower than 20 wt.%. The molar ratio M of the reaction mixture is preferably between 1 and 2.2, more preferably between 1.1 and 1.9.

The molar ratio M of the reaction mixture is defined as $(n_{\text{SO}_3} + n_{\text{H}_2\text{SO}_4})/n_{\text{cap}}$, wherein n_{SO_3} = quantity of SO_3 in reaction mixture, in mol (1 mol SO_3 corresponds to 80 g), $n_{\text{H}_2\text{SO}_4}$ = quantity of H_2SO_4 in reaction mixture, in mol (1 mol H_2SO_4 corresponds to 98 g) and n_{cap} = quantity of caprolactam in reaction mixture, in mol (1 mol caprolactam corresponds to 113 g). With SO_3 content (wt.%) is meant the amount of SO_3 (g) relative to the total amount (g) of reaction mixture comprising sulfuric acid, SO_3 and caprolactam. As used herein, the values for M and the concentration of SO_3 and the temperature of the reaction mixture refer in particular to the values in the reaction mixture obtained after feeding of the cyclohexanone oxime into the reaction mixture.

The values for M and the SO_3 content may be obtained in any suitable way. In a preferred embodiment, the process is a continuous process

- 4 -

comprising keeping the reaction mixture in circulation, feeding oleum to the circulating reaction mixture, feeding oleum to the circulating reaction mixture, and withdrawing part of the circulating reaction mixture. The amount of oleum and the SO_3 content of the oleum fed to the circulating reaction mixture may be chosen such that M and the SO_3 content of the reaction mixture have the preferred values.

The temperature at which the Beckmann rearrangement is carried out is preferably between 70 and 130 °C, more preferably at a temperature of between 70 and 120 °C.

In the process of the invention, the rearrangement is carried out in a plurality of stages connected in series in which the molar ratio M of the reaction mixture preferably decreases in each further step. Preferably, the rearrangement is carried out in at least two stages and more preferably in at least three stages connected in series. Each of these stages is charged with cyclohexanone oxime, while preferably all the oleum required is charged into the first stage. Advantageously, cyclohexanone oxime is fed to each stage with an amount decreasing from stage to stage. This is advantageous as, due to the lower molar ratio in each further stage, the yield to caprolactam decreases in each further stage. Feeding cyclohexanone oxime to each stage with an amount decreasing from each stage results in that the overall high yield to caprolactam is maintained with a comparable lower AS by-product formation. In a more stage rearrangement, the Beckmann rearrangement in each stage is preferably carried out in a circulating reaction mixture comprising caprolactam, sulfuric acid and SO_3 by continuously feeding cyclohexanone oxime and, separately therefrom, oleum (first stage) resp. the amount of the circulating reaction mixture withdrawn from the previous stage (if any) to the circulating reaction mixture and by continuously withdrawing a amount of the circulating reaction mixture equivalent to the amount of cyclohexanone oxime and the amount of oleum (first stage) resp. the amount of the circulating reaction mixture withdrawn from the previous stage (if any) introduced to the circulating reaction mixture and by continuously feeding said amount to the next stage (if any). In the last stage of a more stage rearrangement a portion of the circulating reaction mixture is withdrawn equivalent to the amount of cyclohexanone oxime and the amount of the circulating reaction mixture withdrawn from the previous stage introduced into the circulating reaction mixture of the last stage; from said portion caprolactam is recovered.

In one embodiment of the invention, the rearrangement is carried out in two stages connected in series. In this embodiment, caprolactam is preferably

- 5 -

obtained by a continuous process comprising

- a) feeding (i) oleum and (ii) cyclohexanone oxime into a first circulating reaction mixture comprising caprolactam, sulfuric acid and SO_3 ,
- b) feeding (iii) a portion of the first circulating reaction mixture and (iv) cyclohexanone oxime into a second circulation reaction mixture comprising caprolactam, sulfuric acid and SO_3 , wherein the molar ratio M of the second circulating circulation reaction mixture is between 1.0 and 1.4 and the SO_3 content of the second circulation reaction mixture is higher than 6 wt.%, more preferably higher than 8 wt.% and even more preferably higher than 10 wt.%,
- c) withdrawing a portion of the second circulation reaction mixture from which caprolactam is recovered.

In such two stage rearrangement, preferably, from 60 to 95 by weight of the total amount (fed to the first and second reaction mixture) of cyclohexanone oxime and all of the oleum is fed to the first reaction mixture. The molar ratio M in the first circulating reaction mixture is preferably maintained between 1.2 and 2.2 and the SO_3 concentration is preferably maintained between 3 and 20 wt.%, more preferably higher than 5 wt.% and even more preferably higher than 6 wt.%. The molar ratio M in the first circulating reaction mixture is more preferably maintained between 1.4 and 1.9 and the SO_3 concentration is preferably maintained between 3 and 20 wt.%, more preferably higher than 5 wt.% and even more preferably higher than 6 wt.%. The molar ratio M in the first circulating reaction mixture is even more preferably maintained between 1.5 and 1.8 and the SO_3 concentration is preferably maintained between 3 and 20 wt.%, more preferably higher than 5 wt.% and even more preferably higher than 6 wt.%. The SO_3 concentration in the first circulating reaction mixture is preferably lower than 20 wt.%, more preferably lower than 18 wt.% and even more preferably lower than 17 wt.%. The temperature at which the Beckmann rearrangement is carried out in the first stage is preferably between 70 and 130°C, preferably between 70 and 120 °C. Preferably, from 5 to 40 by weight of the total amount of cyclohexanone oxime (fed to the first and second reaction mixture) is fed to the second reaction mixture. The molar ratio M in the second circulating reaction mixture is preferably maintained between 1 and 1.6 and the SO_3 concentration is preferably maintained between 2 and 20 wt.%, more preferably higher than 6 wt.% and even more preferably higher than 8 wt.%. The molar ratio M in the second circulating reaction mixture is more preferably maintained between 1.2 and 1.4 and the SO_3 concentration is preferably maintained between 2 and 20 wt.%, more preferably higher than 6 wt.% and even more preferably

- 6 -

higher than 8 wt.%. The SO_3 concentration in the second circulating reaction mixture is preferably lower than 18 wt.% and even more preferably lower than 16 wt.%. The temperature at which the Beckmann rearrangement is carried out in the second stage is preferably between 70 and 130°C and more preferably between 80 and 120°C.

- 5 In an even more preferred embodiment of the invention, the rearrangement is carried out in three stages connected in series. In this embodiment, caprolactam is obtained by a continuous process comprising
- a) feeding (i) oleum and (ii) cyclohexanone oxime into a first circulation reaction mixture comprising caprolactam, sulfuric acid and SO_3 ,
- 10 b) feeding (iii) a portion of the first circulation reaction mixture and (iv) cyclohexanone oxime into a second circulation reaction mixture comprising caprolactam, sulfuric acid and SO_3 ,
- c) withdrawing a portion of the second circulation reaction mixture,
- 15 feeding (v) a portion of the second circulation reaction mixture and (vi) cyclohexanone oxime into a third circulation reaction mixture comprising caprolactam, sulfuric acid and SO_3 , wherein the molar ratio M of the third circulation reaction mixture is between 1.0 and 1.4 and the SO_3 content of the third circulation reaction mixture is higher than 6 wt.%, more preferably higher than 8 wt.% and even more preferably higher than 10 wt.%,
- 20 d) withdrawing a portion of the third circulation reaction mixture from which caprolactam is recovered.

In such three stage rearrangement, preferably, from 60 to 95 by weight of the total amount of cyclohexanone oxime (fed to the first, second and third reaction mixture) and all of the oleum are introduced into the first reaction mixture. The

25 molar ratio M in the first circulating reaction mixture is preferably maintained between 1.2 and 2.2 and the SO_3 concentration is preferably maintained between 3 and 20 wt.%, more preferably higher than 5 wt.% and even more preferably higher than 6 wt.%. The molar ratio M in the first circulating reaction mixture is more preferably maintained between 1.4 and 1.9 and the SO_3 concentration is preferably maintained

30 between 3 and 20 wt.%, more preferably higher than 5 wt.% and even more preferably higher than 6 wt.%. The molar ratio M in the first circulating reaction mixture is even more preferably maintained between 1.5 and 1.8 and the SO_3 concentration is preferably maintained between 3 and 20 wt.%, more preferably higher than 5 wt.% and even more preferably higher than 6 wt.%. The SO_3 concentration in the first circulating

35 reaction mixture is preferably lower than 20 wt.%, more preferably lower than 18 wt.%

- 7 -

and even more preferably lower than 17 wt.%. The temperature at which the Beckmann rearrangement is carried out in the first stage is preferably between 70 and 130°C, preferably between 70 and 120 °C. Preferably, from 5 to 40 by weight of the total amount of cyclohexanone oxime (fed to the first, second and third reaction mixture) is fed to the second reaction mixture. The molar ratio M in the second circulating reaction mixture is preferably maintained between 1 and 1.6 and the SO₃ concentration is preferably maintained between 2 and 20 wt.%, more preferably higher than 6 wt.% and even more preferably higher than 8 wt.%. The molar ratio M in the second circulating reaction mixture is more preferably maintained between 1.2 and 1.5 and the SO₃ concentration is preferably maintained between 2 and 20 wt.%, more preferably higher than 6 wt.% and even more preferably higher than 8 wt.%. The SO₃ concentration in the second circulating reaction mixture is preferably lower than 18 wt.% and even more preferably lower than 16 wt.%. The temperature at which the Beckmann rearrangement is carried out in the second stage is preferably between 70 and 130°C and more preferably between 80 and 120°C. Preferably, from 2 to 15 by weight of the total amount of cyclohexanone oxime (fed to the first, second and third reaction mixture) is fed to the third reaction mixture. The molar ratio M in the third circulating reaction mixture is preferably maintained between 1 and 1.4 and the SO₃ concentration is preferably maintained between 4 and 18 wt.%, more preferably higher than 6 wt.% and even more preferably higher than 8 wt.%. The molar ratio M in the third circulating reaction mixture is more preferably maintained between 1.0 and 1.3 and the SO₃ concentration is preferably maintained between 4 and 18 wt.%, more preferably higher than 6 wt.% and even more preferably higher than 8 wt.%. The SO₃ concentration in the third circulating reaction mixture is preferably lower than 17 wt.% and even more preferably lower than 16 wt.%. The temperature at which the Beckmann rearrangement is carried out in the third stage is preferably between 80 and 130°C and more preferably between 80 and 120°C.

Preferably, oleum is continuously introduced into the first circulating reaction mixture in an amount sufficient to maintain the molar ratio M of the circulating reaction mixture in at least the last stage of the more stage rearrangement between 1 and 1.4. The SO₃ content of the oleum introduced into the first circulating reaction mixture is such that the SO₃ content of the circulating reaction mixture in at least the last stage is preferably higher than 6 wt.%, more preferably higher than 8 wt.% and even more preferably higher than 10 wt.%. Preferably, the oleum used in such two or three stage rearrangement has a sulfur trioxide content of from 18 to 35% by weight.

- 8 -

Working at such low molar ratio and high SO_3 content in especially the last stage of a more stage rearrangement is advantageous as low molar ratios in the last stage of a more stage rearrangement results in the formation of small amounts of ammonium sulfate during subsequent neutralisation while high amounts of SO_3 at such low molar ratio results in an improved yield to caprolactam and additionally results in an improved quality of the obtained caprolactam. Preferably, one part of cyclohexanone oxime is continuously introduced into at least 10 parts of the circulating reaction mixture; more preferably, one part of cyclohexanone oxime is introduced into at least 20 parts of the circulating reaction mixture.

5

10 Cyclohexanone oxime (melt) and, separately therefrom, oleum are preferably introduced via dividers. Preferably cyclohexanone oxime is intensively mixed with the reaction mixture. Suitable methods for admixture cyclohexanone oxime with the reaction mixture are for example described in US-A-3601318 and EP-A-15617. In a preferred embodiment of the invention, cyclohexanone oxime is admixed to the

15 reaction mixture using a mixing device as depicted in figure 2. In figure 2, the mixing device comprises a cylindrical tube 101 that in first part 101a narrows to throat 101b, and beyond throat 101b widens in a second part 101c. The second part 101c of the tube is connected to a second tube 102. In the throat openings 103 are present which are in connection with feed chamber 104. Cyclohexanone oxime is supplied via feed

20 chamber 104, and fed into reaction mixture through openings 103. The mixing device comprises closures 105 with which openings 103 can be opened and closed independently. The mixing device also comprises a baffle 106 opposite to the exit of tube 101. The tube opens into collecting vessel B, having walls 110, overflow 111, and outlet 112. Reaction mixture leaving tube 102 is collected in the collecting vessel B, and leaves collecting vessel B partly via line 112 to be further circulated, and partly via

25 overflow 111 to be fed into a subsequent reaction mixture or for the recovery of caprolactam. In a more preferred embodiment of the invention, the mixing device comprises (i) a tube through which the reaction mixture can flow, and (ii) channels disposed around the tube, said channels opening into the tube, said process

30 comprising: passing the reaction mixture through the tube, and feeding the cyclohexanone oxime into the reaction mixture through one or more of said channels, wherein Re of the reaction mixture > 5000 , preferably higher than 10.000, Re being the Reynolds number as defined by $\rho \cdot V \cdot D / \eta$, wherein

ρ = density (in kg/m^3) of the reaction mixture that is fed to the tube

- 9 -

V = velocity of the reaction mixture, V being defined as W/A , wherein W is the flow rate (in m^3/s) of the reaction mixture that is fed into the tube and A is the cross section area of the tube (in m^2) at the level where said channels open into the tube.

- 5 D = diameter of the tube at the level where said channels open into the tube (in m).
 η = viscosity of the reaction mixture that is fed into the tube (in Pa·s).

Preferably, one part of cyclohexanone oxime is continuously introduced into at least 10 parts of the circulating reaction mixture; more preferably, one part of cyclohexanone oxime is introduced into at least 20 parts of the circulating reaction mixture.

- 10 The recovery of caprolactam from the reaction mixture obtained in the last stage of the Beckmann rearrangement may be performed by known methods. Preferably, the reaction mixture obtained in the last stage of the Beckmann rearrangement is neutralized with ammonia in water and the ammonium sulfate thus formed is removed from the caprolactam solution. The caprolactam solution may be purified by known procedures.

Description of preferred embodiment

- Figure 1 shows a preferred set-up for a rearrangement in three stages comprising a first circulation system, a second circulation system and a third circulation system. The first circulation system comprises mixing device A1, collecting vessel B1, pump C1 and cooler D1, and a first reaction mixture is kept in circulation via line 1. The second circulation system comprises mixing device A2, collecting vessel B2, pump C2 and cooler D2, and a second reaction mixture is kept in circulation via line 11. The third circulation system comprises mixing device A3, collecting vessel B3, pump C3 and cooler D3, and a third reaction mixture is kept in circulation via line 21. Cyclohexanone oxime and oleum are fed into the first reaction mixture via line 2 and line 3 respectively. A portion of the first reaction mixture is withdrawn from collecting vessel B1 via line 4 and fed into the second reaction mixture. Cyclohexanone oxime is fed into the second reaction mixture via line 12. A portion of the second reaction mixture is withdrawn from collecting vessel B2 via line 14 and fed into the third reaction mixture. Cyclohexanone oxime is fed to the third reaction mixture via line 24. A portion of the third reaction mixture is withdrawn from collecting vessel B3 via line 34. The process is carried out continuously.

35

- 10 -

Figure 2 shows a mixing device that is preferably used as mixing device A1, mixing device A2, and mixing device A3.

The following specific examples are to be construed as merely illustrative, and not limitative, of the remainder of the disclosure.

- 5 In the examples the yield to caprolactam was determined as follows:
Samples were taken from the reaction mixture leaving the last stage of the rearrangement. The yield (amount of caprolactam formed per amount of cyclohexanone oxime fed to the reaction mixture) was determined as follows: To a first part (0.2 g) of each sample concentrated sulfuric acid (20 ml, 96wt%) was added, as
10 well as 15 g K₂SO₄ and 0.7 g HgO. The nitrogen content of the resulting acidic mixture was determined using the Kjeldahl Method, from which the molar concentration of nitrogen in the first part of the sample (TN) was calculated. A second part of each sample is extracted with chloroform. This method is based on the fact that caprolactam enters the chloroform phase. The impurities stay in the water phase. The extracted
15 aqueous phase is analyzed for its nitrogen content by the Kjeldahl Method, from which the molar concentration of nitrogen in the second part of the sample (RN) was calculated. The yield is calculated as follows:

$$\% \text{ yield} = \left(1 - \frac{RN}{TN}\right) \times 100$$

20

The absorbance at 290 nm (E₂₉₀), used as quality specification of the obtained caprolactam, was determined as follows:

The reaction mixture leaving the last stage of the rearrangement was neutralized with ammonia, and the resulting caprolactam-containing aqueous phase was separated.

- 25 The absorbance of the separated caprolactam-containing aqueous phase was measured at a wavelength of 290 nm using a 1 cm cuvette (calculated for a 70 wt.% aqueous caprolactam solution).

Example 1.

30

This is an example of the preparation of cyclohexanone oxime by reaction of a buffered hydroxylammonium phosphate solution and cyclohexanone in the presence of toluene.

Using the process according to Figure 3, the following hydroxylammonium salt solution was fed to counter-current reactor A via conduit 1, per

- 11 -

unit time:

65 kmoles of $\text{NH}_2\text{OH} \cdot \text{H}_3\text{PO}_4$

97 kmoles of $\text{NH}_4\text{H}_2\text{PO}_4$

38 kmoles of H_3PO_4

- 5 191 kmoles of NH_4NO_3 and
3184 kmoles of H_2O .

10 The said solution was derived from a hydroxylamine synthesis stage in which nitrate ions, supplied in the form of 55% by weight of nitric acid, were reduced to hydroxylamine with the aid of hydrogen in a medium buffered with the aid of a combination of phosphate and phosphoric acid and in the presence of a platinum catalyst. The pH of the solution was 2.1.

A further solution of 65 kmoles of cyclohexanone, and a toluene stream containing:

- 15 400 kmoles of toluene,
9 kmoles of cyclohexanone,
2 kmoles of oxime and
5 kmoles of H_2O ,

were admitted to the said reactor A via the conduits 2 and 3, respectively.

The temperature in the reactor A was maintained at 70°C.

20 An oxime-containing toluene product stream was discharged from the reactor through conduit 4 to column C. The said product stream contained:

- 400 kmoles of toluene,
65 kmoles of oxime and
20 kmoles of H_2O .

25 In column C, separation into oxime and toluene was effected. 65 kmoles of oxime per unit time were discharged via conduit 6, while toluene (400 kmoles) and water (20 kmoles) were discharged to extraction column B via conduit 7.

An aqueous solution was discharged per unit time via conduit 8 to extraction column B containing:

- 30 191 kmoles of NH_4NO_3
97 kmoles of $\text{NH}_4\text{H}_2\text{PO}_4$
103 kmoles of H_3PO_4
9 kmoles of cyclohexanone,
2 kmoles of oxime and
35 3234 kmoles of H_2O .

- 12 -

After removal of toluene dissolved therein by stripping, the aqueous solution discharged from extraction column B had the following composition:

97 kmoles of $\text{NH}_4\text{H}_2\text{PO}_4$

191 kmoles of HN_4NO_3

5 103 kmoles of H_3PO_4 and

3249 kmoles of H_2O .

This solution was recycled to the hydroxylamine synthesis stage to serve as the reaction medium in the reduction of nitric acid to hydroxylamine.

The oxime obtained in column C contains less than 1000 ppm water.

10 Said oxime was used in Examples 2-4 given below.

Comparative Experiment A

A set-up was used as depicted in figures 1 and 2. To the 1st step of a rearrangement system 7.1 t/hr oxim containing 4.7 % water is fed (2) and 9.2 t/hr oleum containing 25 wt.% SO_3 (3). The temperature of the reactor is maintained at 102°C by circulating the rearrangement mixture at a rate of 400 t/hr over a cooler (D1) in which its temperature is lowered to 77°C. The oxime is mixed into the circulating mixture through a mixing device (A1) having a throat diameter of 51 mm (101b) and the mixing device was provided with 16 channels (diameter 3 mm). Cyclohexanone oxime was fed through 8 channels (8 of the channels being in closed position). The velocity of the circulating mixture in the throat is 40 m/s and the velocity at which cyclohexanone oxime is fed to the circulating reaction mixture is 41 m/s. The reactor discharge (4) is sent to the 2nd step of the rearrangement system where 1.9 t/hr oxime of identical origine is added (12). In the second and third step of the rearrangement system the oxime is mixed into the circulating mixture through a mixing device (A1) as used in the first step but of which the dimensions are adapted to the lower throughput in the second and third step. Circulation rate is 150 t/hr and cooler (D2) outlet temperature is 72°C and the reactor operates at 86 °C. Finally the discharge of the 2nd reactor (14) is sent to the 3rd step of the rearrangement sytem where 1.1 t/hr oxime is added (22).
30 Operating temperature is again 86 °C controlled by circulating rate of 100 t/hr and cooler outlet temperature of 76°C.

The molar ratios of the reaction mixtures in the first, second resp. third step are 1.68, 1.32 and 1.18 respectively, which corresponds to weight ratios of 1.46, 1.15 and 1.02 resp. The weight ratio of the reaction mixture is defined as
35 (quantity of SO_3 in reaction mixture + quantity of H_2SO_4 in reaction mixture)/quantity of

- 13 -

caprolactam in reaction mixture. The SO_3 concentration in the reaction mixture in the first, second resp. third step were: 4.8 % , 2.1% and 0.8 % resp. The overall yield of the 3-step rearrangement system was determined using the above given method: 98.9 %. The extinction at 290 nm (determined as given above) was 3.54.

5

Example 2

Comparative Experiment was repeated with the difference that cyclohexanone oxime as prepared according to example 1 was used. The oxime feed rates to the three rearrangement steps were almost identical as in Comparative Experiment A. The oleum feed rate was not adjusted resulting in lower oleum to oxime ratio compared with Comparative Experiment A. Circulation rates were maintained as in Comparative Experiment A and cooling temperatures were slightly adjusted in order to be able to keep the reactor temperatures on a same level as in Comparative Experiment A.

The SO_3 concentration in the reaction mixture of the first, second resp. third step were 14.2 %, 12.7% and 12.0 % resp. and the overall yield measured in the discharge of the 3rd reactor was determined with the above given method to be 99.4%. The extinction at 290 nm (determined as given above) was 0.65.

20 Example 3

Comparative Experiment A was repeated with the difference that cyclohexanone oxime as prepared according to example 1 was used and that, to ensure similar oleum to oxime consumption ratios, the oleum feed was reduced in a way that the molar ratios measured in each of the three steps were close or identical to the values from Comparative Experiment A.

Circulation rates were maintained as in Comparative Experiment A and cooling temperatures were slightly adjusted in order to be able to keep the reactor temperatures on a same level as in Comparative Experiment A.

The SO_3 concentration of the reaction mixture in the first, second resp. third step were 14.5 %, 13.0% and 12.3 % resp. The overall yield measured in the outlet 3rd reactor was determined with the above given method to be 99.5%. The extinction at 290 nm (determined as given above) was 0.38.

Comparing Comparative Experiment A with Example 2 shows that the use of oxime as prepared according to the invention results in an increase of the yield to caprolactam and the quality of the obtained caprolactam. Comparing Example

35

- 14 -

2 with Example 3 shows that the use of oxime as prepared according to the invention makes it possible to reduce the quantity of oleum added per quantity of oxime resulting in a lower molar ratio of the reaction mixture in the last stage (and thus a lower amount of ammonium sulfate in the subsequent neutralization) and the yield to caprolactam and the quality of the obtained caprolactam is further improved.

Example 4

Comparative Experiment was repeated with the difference that oxime as prepared according to example 1 was used and oleum containing less than 9 wt.% SO₃ was used. The oxime feed rates to the three rearrangement steps were left unchanged. To ensure similar oleum to oxime consumption ratios as in Comparative Experiment A the oleum feed rate was eventually set to 10 t/hr as to achieve molar ratios in each of the three steps that are close or identical to the values from Comparative Experiment A.

Circulation rates were maintained as in Comparative Experiment A and cooling temperatures were slightly adjusted in order to be able to keep the reactor temperatures on a same level as in Comparative Experiment A. The SO₃ concentration of the reaction mixture in the first, second resp. third step were 5.0 %, 4.4% and 4.2 % resp. The overall yield measured in the outlet 3rd reactor was determined with the above given method to be 99.3%. The extinction at 290 nm (determined as given above) was 1.06.

Comparing Comparative Experiment A with Example 4 shows that the use of oxime as prepared according to the invention makes it possible to use oleum having a lower SO₃ content while the yield to caprolactam and the quality of the obtained caprolactam is further improved.

- 15 -

CLAIMS

1. A continuous process for preparing caprolactam by Beckmann rearrangement of cyclohexanone oxime, said process comprising
 - 5 a) feeding (i) oleum and (ii) cyclohexanone oxime into a first reaction mixture comprising caprolactam, sulfuric acid and SO_3 ,
 - b) feeding (iii) a portion of the first reaction mixture and (iv) cyclohexanone oxime into a second reaction mixture comprising caprolactam, sulfuric acid and SO_3 ,
 - 10 c) withdrawing a portion of the second reaction mixture, wherein the process further comprises obtaining the cyclohexanone oxime that is fed to the first reaction mixture and second reaction mixture by:
 - 1) preparing an organic medium comprising cyclohexanone oxime dissolved in an organic solvent
 - 15 2) separating, by distillation, cyclohexanone oxime from said organic medium.
2. A process according to claim 1, said process further comprising
 - 20 d) feeding (v) a portion of the second reaction mixture and (vi) cyclohexanone oxime into a third reaction mixture comprising caprolactam, sulfuric acid and SO_3 , and
 - e) withdrawing a portion of the third reaction mixture.
3. Process according to any one of claims 1-2, wherein the cyclohexanone oxime contains less than 1 wt.% water.
4. Process according to any one of claims 1-3, wherein the cyclohexanone oxime contains less than 0.1 wt.% water.
- 25 5. Process according to any one of claims 1-4, wherein the SO_3 content of the reaction mixture comprising caprolactam, sulfuric acid and SO_3 is at least 6 wt.%.
6. Process according to any one of claims 1-5, wherein the SO_3 content of the reaction mixture comprising caprolactam, sulfuric acid and SO_3 is at least 8 wt.%.
- 30 7. Process according to any one of claims 1-6, wherein the SO_3 content of the reaction mixture comprising caprolactam, sulfuric acid and SO_3 is at least 10 wt.%.
- 35 8. Process according to any one of claims 1-7, wherein each reaction mixture is

- 16 -

- 5 kept in circulation in a separate circulation system and wherein oleum is continuously introduced into the first circulating reaction mixture in an amount sufficient to maintain the molar ratio M of the circulating reaction mixture of the last stage between 1 and 1.4 and wherein the SO_3 content of the oleum introduced into the first circulating reaction mixture is such that the SO_3 content of the circulating reaction mixture in the last stage is between 9 and 20 wt. %
9. Process according to claim 8, wherein the SO_3 content of the oleum is between 18 and 35 wt. %

10

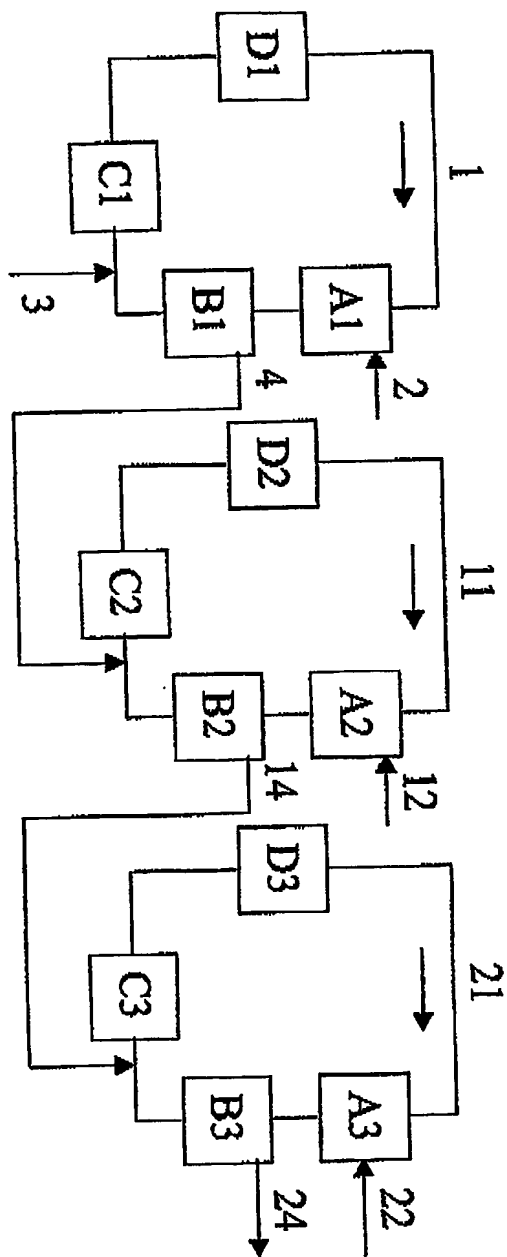
- 17 -

ABSTRACT

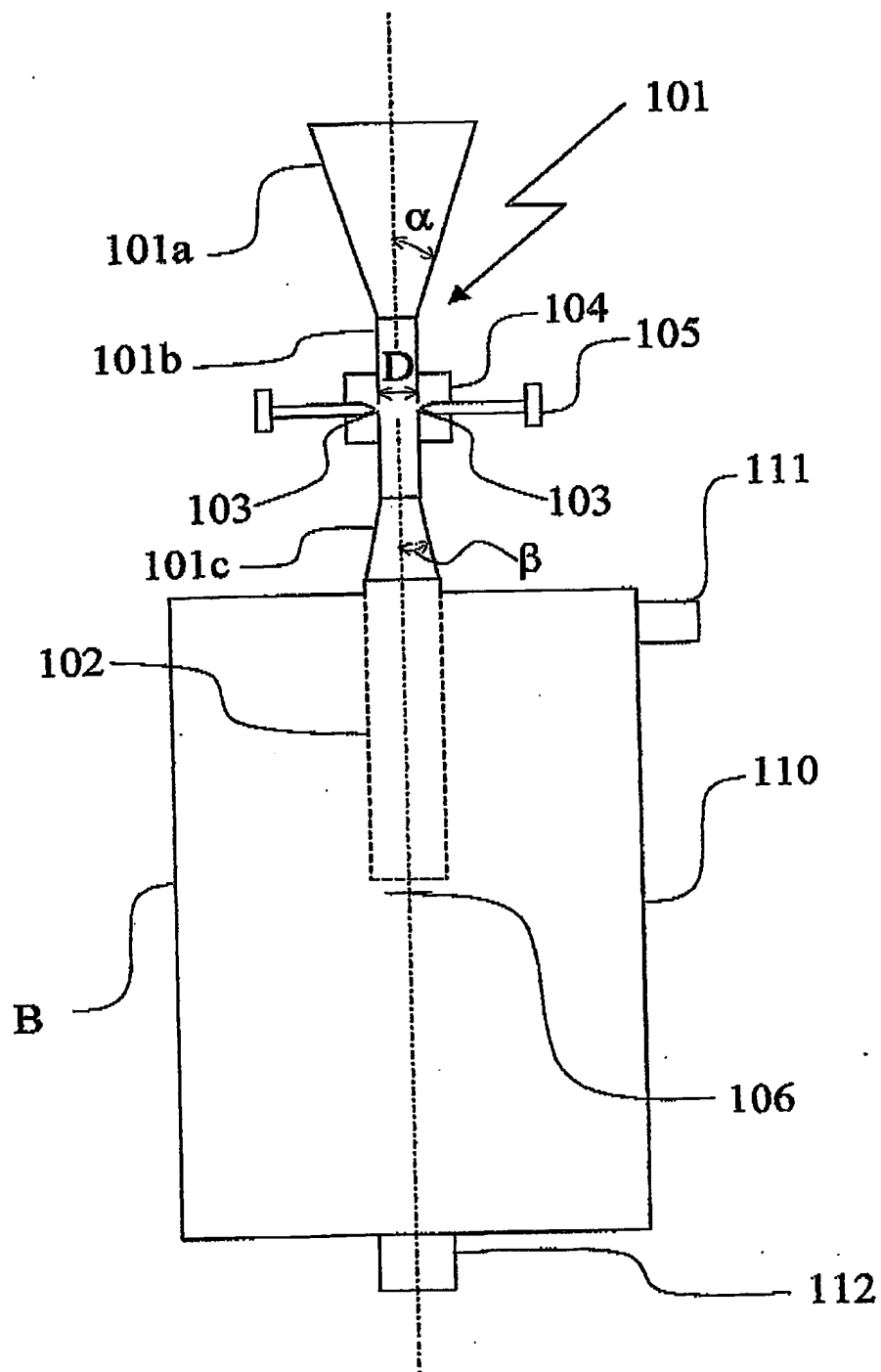
The invention relates to a continuous process for preparing caprolactam by Beckmann rearrangement of cyclohexanone oxime, said process comprising

- 5 a) feeding (i) oleum and (ii) cyclohexanone oxime into a first reaction mixture comprising caprolactam, sulfuric acid and SO_3 ,
b) feeding (iii) a portion of the first reaction mixture and (iv) cyclohexanone oxime into a second reaction mixture comprising caprolactam, sulfuric acid and SO_3 ,
c) withdrawing a portion of the second reaction mixture, wherein the process further
10 comprises obtaining the cyclohexanone oxime that is fed to the first reaction mixture and second reaction mixture by:
1) preparing an organic medium comprising cyclohexanone oxime dissolved in an organic solvent
2) separating, by distillation, cyclohexanone oxime from said organic medium.

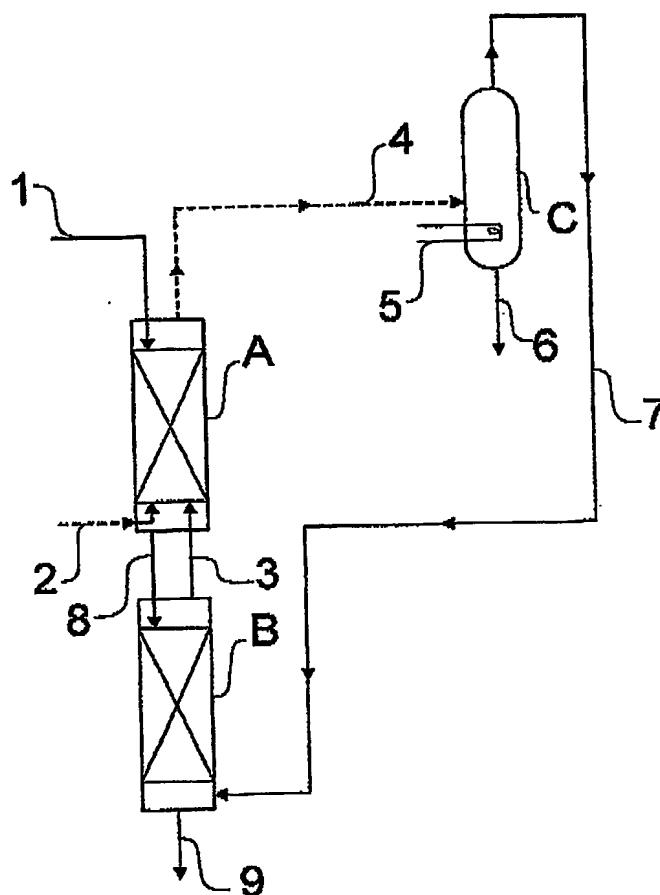
- 1/3 -



- 2/3 -



- 3/3 -



PCT/EP2004/005643

